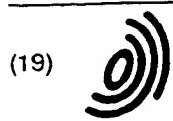


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(71) Applicant:  
DAINIPPON INK AND CHEMICALS, INC.  
Itabashi-ku Tokyo (JP)

(72) Inventor: Nagata, Yoshitomo  
Sakura-shi, Chiba (JP)

(74) Representative:  
Kraus, Walter, Dr. et al  
Patentanwälte Kraus, Weisert & Partner  
Thomas-Wimmer-Ring 15  
80539 München (DE)

(54) Separation membrane

(57) Separation membranes excellent in strength, durability, heat resistance and solvent resistance as well as in balance between substance separation properties and substance permeability are disclosed, which are formed from polyhydrazidoimide resins, and preferably comprises a non-porous dense layer formed from a polyhydrazidoimide resin obtained from the reaction of an aromatic tetracarboxylic dianhydride such as 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and an aromatic dihydrazide such as isophthalic dihydrazide as essential components.

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## SUMMARY OF THE INVENTION

An object of the present invention is to provide a separation membranes excellent in strength, durability, heat resistance and solvent resistance having an excellent balance between substance separation properties and permeability to substances.

The inventor made extensive studies paying their attention to polyhydrazidoimide resins as polymers containing hydrazidoimide structure which having the nitrogen atom in the imide ring and the nitrogen atom in the amide bond which are directly connected to each other, in the repeating unit to obtain better separation membranes as compared with polyimides or the like. As a result, it was found that polyhydrazidoimide resins are excellent in properties such as strength, durability, heat resistance and solvent resistance similarly to polyamideimides containing imide bonds and amide bonds and exhibits a good balance between separation properties and permeability, excellent particularly in gas separation properties, as compared with these resins. Thus, the present invention has been worked out.

In other words, in order to accomplish the foregoing objects, the present invention provides:

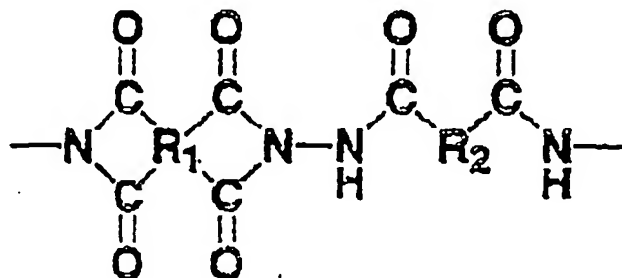
- (1) Separation membranes formed from polyhydrazidoimide resins;
- (2) The separation membrane according to Clause (1), having a non-porous dense layer formed from polyhydrazidoimide resins;
- (3) The separation membranes according to Clause (2), which are gas-separation membranes;
- (4) The separation membranes according to Clause (2), having a composite structure comprising a non-porous dense layer formed from polyhydrazidoimide resins and a porous supporting layer formed from materials different from the resin constituting said non-porous dense layer;
- (5) The separation membranes according to any one of Clauses (1) to (4), wherein said polyhydrazidoimide resins are polymers obtained from the reaction of aromatic tetracarboxylic dianhydrides and aromatic dihydrazides as essential components;
- (6) The separation membranes according to Clause (5), wherein said aromatic tetracarboxylic dianhydride is 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; and
- (7) The separation membranes according to Clause (5), wherein said aromatic dihydrazide is isophthalic dihydrazide or terephthalic dihydrazide.

## BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph illustrating the relationship between the oxygen permeability coefficient and the oxygen/nitrogen separation factor of the various dense symmetrical membranes obtained in Examples 1 to 9 and Comparative Examples 1 to 3.

## DETAILED DESCRIPTION OF THE INVENTION

The polyhydrazidoimide resins to be used in the present invention are polymer compounds containing in their repeating unit the structure (hydrazidoimide structure) represented by the following general formula (1):



wherein  $R_1$  represents a tetra-substituted residue; and  $R_2$  represents a di-substituted residue, in which structure the nitrogen atom in the imide ring and the nitrogen atom in the amide bond are directly bonded to each other. In the general formula (1),  $R_1$  is preferably a tetra-substituted residue having aromatic, heterocyclic or alicyclic rings, more preferably tetra-substituted residues represented by the following general formula:

diester dichloride having rings such as aromatic ring, heterocyclic ring and alicyclic ring are preferred. These tetracarboxylic acids may be used singly or in admixture.

Preferred among these tetracarboxylic acids is tetracarboxylic dianhydride. Examples of the tetracarboxylic dianhydride include aromatic tetracarboxylic dianhydride such as pyromellitic dianhydride (hereinafter referred to as "PMDA"), 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-diphenylethertetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride, 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride (hereinafter referred to as "6FDA"), 4,4'-methylenediphthalic anhydride, 4,4'-ethylenediphthalic anhydride, 4,4'-isopropylidenediphthalic anhydride, azobenzenetetracarboxylic dianhydride, naphthalene-1,4,5,8-tetracarboxylic dianhydride, anthracenetetracarboxylic dianhydride and perylene-3,4,9,10-tetracarboxylic dianhydride; heterocyclic tetracarboxylic dianhydride such as pyridinetetracarboxylic dianhydride, thiophenetetracarboxylic dianhydride and furantetracarboxylic dianhydride; and alicyclic tetracarboxylic dianhydride such as cyclobutane tetracarboxylic dianhydride, cyclopentanetetracarboxylic dianhydride, cyclohexanetetracarboxylic dianhydride and bicyclooctenetetracarboxylic dianhydride. Preferred among these tetracarboxylic dianhydrides are aromatic tetracarboxylic dianhydrides. Most preferred among these aromatic tetracarboxylic dianhydrides is 6FDA, which provides excellent gas permselectivity and good solubility characteristics.

The dihydrazides to be used in the preparation of the polyhydrazidoimide resin are not specifically limited. In practice, however, dihydrazides having rings such as aromatic ring, heterocyclic ring and alicyclic ring are preferred. Particularly preferred among these dihydrazides are aromatic dihydrazides. Examples of such aromatic dihydrazides include phthalic dihydrazide (e.g., isophthalic dihydrazide and terephthalic dihydrazide), naphthalenedicarboxylic dihydrazide (e.g., 2,6-naphthalene dicarboxylic dihydrazide), hydroxyisophthalic dihydrazide, dimethylterephthalic dihydrazide, biphenyldicarboxylic dihydrazide, benzophenonedicarboxylic dihydrazide, diphenyletherdicarboxylic dihydrazide, diphenylsulfonedicarboxylic dihydrazide, hexafluoroisopropylidenediphthalic dihydrazide. Most preferred among these aromatic dihydrazides are isophthalic dihydrazide, terephthalic dihydrazide and 2,6-naphthalene dicarboxylic dihydrazide.

The polydihydrazidoimide resins to be used in the present invention may be copolymers of dihydrazides with copolymerizable compounds such as diamine, triamine and tetraamine. Examples of such copolymers include amide, imide and/or imidazopyrrolone copolymers.

The copolymerizable compounds are not specifically limited. In practice, however, amino compounds to be used in the synthesis of polyimides, polyimidazopyrrolones, etc. are preferred. Examples of such diamine include phenylenediamine-derivatives such as phenylenediamine (e.g., m-phenylenediamine, p-phenylenediamine) and compounds obtained by substituting some of hydrogen atoms in the benzene ring in these phenylenediamines by alkyl groups, carboxyl groups, hydroxyl groups, alkoxy groups, nitro groups, halogen atoms, etc. (e.g., 2,4-diaminotoluene, 2,5-dimethyl-1,4-phenylenediamine, 2,4,6-trimethyl-1,3-phenylenediamine, 3,5-diaminobenzoic acid, 2,4-diaminophenol, 2,4-diaminonitrobenzene, 2-chloro-5-methyl-1,4-phenylenediamine); aromatic diamines such as compounds having two of more biphenyl-bonded benzene rings, compounds having two or more benzene rings bonded to each other via ether bonds, thioether bonds, carbonyl groups, sulfone groups, sulfide groups, methylene groups, isopropylidene groups, hexafluoroisopropylidene groups, amino groups, amide bonds, etc., compounds obtained by substituting some of hydrogen atoms in the benzene rings in these diamino compounds by alkyl groups, aryl groups, carboxy groups, hydroxy groups, alkoxy groups, nitro groups, halogen atoms, etc. (e.g., 3,3'-dimethylbenzidine, 3,3',5,5'-tetramethylbenzidine, 3,3'-dihydroxybenzidine, dianisidine, 3,3'-dichlorobenzidine, 3,3'-diamino-4,4'-dihydroxybiphenyl, 4,4'-diaminodiphenylether, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylsulfide, 4,4'-diaminodiphenylmethane, 4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane, 4,4'-diamino-3,3'-dicarboxydiphenylmethane, 2,2-bis(4-(4-aminophenoxy)-3,5-dibromophenyl)propane, 9,9-bis(4-aminophenyl)fluorene, 2,2-bis(4-aminophenyl)hexafluoropropane, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 4,4'-diaminobenzanilide, 1,5-naphthalenediamine, 2,7-diaminofluorene and 3,3'-dimethylnaphthidine; heterocyclic diamines such as 2,6-diaminopyridine and diaminocarbazole; triamines such as 1,2,4-triaminobenzene and 3,4,4'-triaminobiphenylether; and tetramines such as 1,2,4,5-tetraminobenzene and 3,3',4,4'-tetraminobiphenyl.

Preferred among these amines are amines having an aromatic ring. Particularly preferred among these amines having aromatic rings are p-phenylenediamine, 2,4-diaminotoluene, 2,5-dimethyl-1,4-phenylenediamine, 2,4,6-trimethyl-1,3-phenylenediamine, 3,3'-dimethylbenzidine, 3,3',5,5'-tetramethylbenzidine, 4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane, 9,9-bis(4-aminophenyl)fluorene, 2,2-bis(4-aminophenyl)hexafluoropropane, 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, 1,5-naphthalenediamine, 3,3'-dimethylnaphthidine, 1,2,4-triaminobenzene, 3,4,4'-triaminobiphenylether, 1,2,4,5-tetraaminobenzene, and 3,3',4,4'-tetraaminobiphenyl.

Among the polyhydrazidoimide resins employable in the present invention, the polyhydrazidoimide resin free of copolymerizable components exhibit an excellent gas permeation selectivity with respect to various gases as compared with known polyimides and polyamideimides. Further, referring to polyhydrazidoimide resins comprising copolymeriza-

soluble polyvalent alcohols such as ethylene glycol and glycerin; and inorganic salts such as lithium chloride, lithium bromide, potassium chloride, potassium bromide, calcium chloride and magnesium chloride.

As the fluid to be used as the core fluid when the dope is extruded into a hollow fiber there may be used gases or liquids. For example, gases such as nitrogen and air or liquids such as water, methanol, ethanol, propanol, glycerin and mixture thereof may be used. If necessary, the core fluid may comprise inorganic salts such as lithium chloride, lithium bromide and potassium chloride, solvents for the resin such as N-methyl pyrrolidone and N,N-dimethyl acetamide, poor solvents for the dope resin such as acetone, methyl ethyl ketone, xylene, toluene, acetic acid and propionic acid, etc. incorporated therein in a proper amount.

The atmosphere in which the dope is extruded may be a gas phase such as air, nitrogen or solvent vapor or a liquid phase such as water, preferably a gas phase. Referring to the atmosphere, the air stream can be properly controlled. If necessary, the temperature and humidity can be properly controlled.

The single layer or multi-layer dope which has been extruded through the multiple tubular capillary nozzle into a hollow fiber is then allowed to come in contact with a coagulating bath to undergo coagulation. As the coagulating bath there may be used any liquid in which the resin constituting the hollow fiber membrane is insoluble but with which the solvent used for the dope is miscible. Examples of such a coagulating bath include lower alcohols such as methanol, ethanol, 1-propanol and 2-propanol; ketones such as acetaldehyde and acetone; water; and mixture thereof. The coagulating bath may comprise substances such as organic solvent, salt, acid and alkali incorporated therein. Preferred among these coagulating baths are water and a mixture of water with other organic solvents.

If the separation membrane of the present invention is a composite membrane, i.e., if the material constituting the non-porous dense layer is different from that constituting the porous layer, the material constituting the porous supporting layer is arbitrary. In some detail, any resins other than polyhydrazidoimide resin may be used so far as they can be thoroughly bonded to the non-porous dense layer made of polyhydrazidoimide resins and exhibit mechanical strength, heat resistance, chemical resistance and weather resistance sufficient for practical use of the membrane. The material may be a mixture or copolymer of two or more such resins. The polyhydrazidoimide resin has a good adhesivity (miscibility) with other polymers. If the polyhydrazidoimide resin is formed into a hollow fiber composite membrane, the degree of freedom of selection of the material constituting the porous supporting layer is high. Therefore, by selecting proper materials for this purpose, high performance separation membranes can be provided.

Preferred examples of the resin from which the foregoing porous supporting layer is prepared include polyamide resin, polyimide resin, polyetherimide resin, polyamideimide resin, polysulfone resin, polybenzimidazole resin, polybenzoxazole resin, polybenzthiazole resin, polyquinoxaline resin, and polypiperazine resin. These resins may be used singly or in admixture.

Examples of the foregoing polysulfone resin include polysulfone, polyethersulfone, polyallylsulfone, and polyphenylsulfone. Various polysulfone resins are commercially available.

The non-porous dense layer can be formed on the inner surface and/or outer surface of the hollow fiber by properly selecting the composition, concentration and temperature of the dope, the composition of the coagulating bath, the composition of the inner fluid, the spinning conditions, etc., if the membrane is a hollow fiber membrane, or by changing the order of the foregoing dopes (a) and (b) to be arranged from the core side, if the membrane is a composite hollow fiber membrane. In particular, the composite membrane having a dense layer formed on the outer surface of the hollow fiber can be easily mass-produced and exhibits an excellent gas permeation selectivity. The dimension of the hollow fiber membrane is arbitrary and can be properly adjusted to outer diameter, inner diameter and other factors suitable for practical use. In some detail, by control the composition, concentration and temperature of the dope, the composition of the coagulating bath, the composition of the inner fluid, the spinning conditions (dope extrusion rate, winding speed of hollow fiber formed, etc.), etc., hollow fibers having, e.g., an outer diameter of not more than 1,500  $\mu\text{m}$  and a thickness of not more than 500  $\mu\text{m}$  can be prepared.

It is preferred that the organic solvent remaining in the membrane thus obtained be substantially removed. The removal of the remaining organic solvent can be accomplished, e.g., by a process which comprises washing the membrane with hot water and/or a volatile solvent which dissolves the organic solvent therein so that the remaining organic solvent is replaced by water or the volatile solvent, and then drying the membrane in vacuo.

Examples of the volatile solvent which dissolves the remaining organic solvent therein include methanol, ethanol, and 2-propanol.

The preparation of the separation membrane of the present invention can be accomplished by a process which comprises preparing a membrane having a non-porous dense layer made of a polyhydrazidoimide resin precursor from a polyhydrazidoimide resin precursor as a dope of non-porous dense layer in the same manner as described above, and then subjecting the membrane to heat treatment so that the polyhydrazidoimide resin precursor is cyclized into hydrazidoimide. This process is particularly useful when the polyhydrazidoimide resins cannot be dissolved or can hardly be dissolved in organic solvents, making them impossible to form a dope. If a precursor of polyhydrazidoimide resin containing copolymerizable components is used, the copolymerizable components may be heated at the same time so that they are subjected to cyclization into imide, imidazopyrrolone or the like.

doimide was obtained. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor calculated is set forth in Table 1.

### EXAMPLE 3

4.086 g (0.03 mol) of 2,5-dimethyl-1,4-phenylenediamine was dissolved as a copolymerizable compound in 350 g of dehydrated N-methylpyrrolidone at room temperature in a nitrogen atmosphere. 13.593 g (0.07 mol) of isophthalic dihydrazide was then suspended in the solution obtained. To the suspension obtained was then added batchwise 44.424 g (0.1 mol) of 4,4'-(hexafluoro isopropylidene)diphthalic anhydride. The reaction mixture was then subjected to reaction and treatment in the same manner as in Example 1 to obtain a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyhydrazidoimide resin containing a copolymerizable component. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor calculated is set forth in Table 1.

### EXAMPLE 4

4.746 g (0.03 mol) of 1,5-naphthalenediamine was dissolved as a copolymerizable compound in 350 g of dehydrated N-methylpyrrolidone at room temperature in a nitrogen atmosphere. 13.593 g (0.07 mol) of isophthalic dihydrazide was then suspended in the solution obtained. To the suspension obtained was then added batchwise 44.424 g (0.1 mol) of 4,4'-(hexafluoro isopropylidene)diphthalic anhydride. The reaction mixture was then subjected to reaction and treatment in the same manner as in Example 1 to obtain a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyhydrazidoimide resin containing a copolymerizable component. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor calculated is set forth in Table 1.

### EXAMPLE 5

9.373 g (0.03 mol) of 3,3'-dimethylnaphthidine was dissolved as a copolymerizable compound in 350 g of dehydrated N-methylpyrrolidone at room temperature in a nitrogen atmosphere. 13.593 g (0.07 mol) of isophthalic dihydrazide was then suspended in the solution obtained. To the suspension obtained was then added batchwise 44.424 g (0.1 mol) of 4,4'-(hexafluoro isopropylidene)diphthalic anhydride. The reaction mixture was then subjected to reaction and treatment in the same manner as in Example 1 to obtain a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyhydrazidoimide resin containing a copolymerizable component. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor thus calculated is set forth in Table 1.

### EXAMPLE 6

4.086 g (0.03 mol) of 2,5-dimethyl-1,4-phenylenediamine was dissolved as a copolymerizable compound in 350 g of dehydrated N-methylpyrrolidone at room temperature in a nitrogen atmosphere. 13.593 g (0.07 mol) of terephthalic dihydrazide was then suspended in the solution obtained. To the suspension thus obtained was then added batchwise 44.424 g (0.1 mol) of 4,4'-(hexafluoro isopropylidene)diphthalic anhydride. The reaction mixture was then subjected to reaction and treatment in the same manner as in Example 1 to obtain a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyhydrazidoimide resin containing a copolymerizable component. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor thus calculated is set forth in Table 1.

### EXAMPLE 7

9.710 g (0.05 mol) of isophthalic dihydrazide and 10.714 g (0.05 mol) of 3,3',4,4'-tetraaminobiphenyl as a copolymerizable compound were dissolved in 200 g of dehydrated N-methylpyrrolidone at room temperature in a nitrogen atmosphere. The solution obtained was then diluted with 150 g of sulfolane. To the solution thus obtained was then added batchwise 44.424 g (0.1 mol) of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. After 4,4'-(hexafluoroisopropylidene)diphthalic anhydride was visually confirmed to undergo almost complete dissolution, 33.142 g (0.2 mol) of tetraethylammonium chloride was added to the solution as a reaction aid. The reaction solution was then allowed to undergo reaction with stirring for 2 hours. The reaction solution thus obtained was then added dropwise to a large amount of isopropyl alcohol. The solid matter precipitated was washed with a large amount of water several times. The water content in the solid matter was then thoroughly replaced by isopropyl alcohol. The solid matter was then dried at a temperature of 100°C in vacuo to obtain a purified polyhydrazidoimide resin precursor polymer containing a copolymerizable component.

A 20% N-methylpyrrolidone solution of the precursor polymer obtained was then prepared. The solution was cast

## COMPARATIVE EXAMPLE 2

The procedure of Comparative Example 1 was followed except that 22.727 g (0.1 mol) of 4,4'-diaminobenzanilide was used instead of p-phenylenediamine. As a result, a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyamideimide. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor calculated is set forth in Table 1.

The polyamideimide used in Comparative Example 2 was synthesized in the same manner as in Example 2 except that 4,4'-diaminobenzanilide, which is an amide-containing diamine, was used instead of terephthalic dihydrazide. This resin has a structure similar to that of the polyhydrazidoimide of Example 2. However, it is obvious that the dense symmetric membrane prepared from this resin is inferior to that prepared from the polyhydrazidoimide obtained in Example 2 in permeation selectivity as shown in Fig. 1. This shows that the simple occurrence of both amide and imide components is not sufficient to exert an effect of providing a high selectivity. Thus, it can be understood that the hydrazidoimide structure is superior over other structures.

## COMPARATIVE EXAMPLE 3

The procedure of Comparative Example 1 was followed except that 21.624 g (0.1 mol) of 3,3'-diamino-4,4'-dihydroxybiphenyl was used instead of p-phenylenediamine. As a result, a 25- $\mu$ m thick film-like dense symmetric membrane made of a polyimide. The membrane was measured for oxygen and nitrogen permeability coefficients. The oxygen/nitrogen separation factor calculated is set forth in Table 1.

The polyimide used in Comparative Example 3 has almost the same oxygen permeability as that of the polyhydrazidoimide resin of Example 3 or 4. However, Fig. 1 shows that the dense symmetric membrane formed from the polyimide used in Comparative Example 3 is inferior to that formed from polyhydrazidoimides in permeation selectivity. Thus, it can be understood that the polyhydrazidoimide structure is superior over other structures.

Table 1

		Gas permeability coefficient (barrier)		Separation factor Oxygen/nitrogen
		Oxygen	Nitrogen	
Example	1	0.641	0.0803	7.98
	2	0.635	0.0794	8.00
	3	1.24	0.174	7.13
	4	1.17	0.164	7.13
	5	1.96	0.282	6.95
	6	1.75	0.248	7.06
	7	2.69	0.368	7.31
	8	1.68	0.240	7.00
	9	0.853	0.120	7.11
Comparative Example	1	4.19	0.784	5.34
	2	2.73	0.457	5.97
	3	1.10	0.173	6.36

## EXAMPLE 10

A 20% dimethylacetamide solution of the polyhydrazidoimide resin obtained in Example 1 was filtered through a stainless steel filter having a filter pore diameter of 20  $\mu$ m while being kept at a temperature of 60°C. The filtrate was then defoamed under reduced pressure to obtain a spinning dope (a). Separately, a 27% N-methylpyrrolidone solution of a polyimide ("MATRIMID 5218", available from Asahi-Ciba Limited) was filtered through a stainless steel filter having a filter pore diameter of 20  $\mu$ m while being kept at 60°C. The filtrate was then defoamed under reduced pressure to obtain a spinning dope (b).

available from Asahi-Ciba Limited) to be used as the spinning dope (b) was replaced by a resin solution comprising 10% of "MATRIMID 5218", 15% of a polybenzimidazole and 75% of N-methylpyrrolidone.

The composite hollow fiber membrane obtained was measured for oxygen and nitrogen permeation rates in the same manner as in Example 10. The oxygen/nitrogen separation factor calculated is set forth in Table 2.

#### EXAMPLE 16

A composite hollow fiber membrane was obtained in the same manner as in Example 10 except that the polyhydrazidoimide resin obtained in Example 1 to be used as the resin for the spinning dope (a) was replaced by the polyhydrazidoimide resin obtained in Example 3 and the N-methylpyrrolidone solution of a polyimide ("MATRIMID 5218", available from Asahi-Ciba Limited) to be used as the spinning dope (b) was replaced by a resin solution comprising 17.5% of "MATRIMID 5218", 7.5% of a polyetherimide ("Utem 1000", available from GE Plastics Japan) and 75% of N-methylpyrrolidone.

The composite hollow fiber membrane obtained was measured for oxygen and nitrogen permeation rates in the same manner as in Example 10. The oxygen/nitrogen separation factor calculated is set forth in Table 2.

#### EXAMPLE 17

A composite hollow fiber membrane was obtained in the same manner as in Example 10 except that the polyhydrazidoimide resin obtained in Example 1 to be used as the resin for the spinning dope (a) was replaced by the precursor polymer of polyhydrazidoimide resin obtained in Example 7 and the N-methylpyrrolidone solution of a polyimide ("MATRIMID 5218", available from Asahi-Ciba Limited) to be used as the spinning dope (b) was replaced by a resin solution comprising 15% of "MATRIMID 5218" and 85% of a polyimide solution ("Rikacoat SN20", available from New Japan Chemical Co., Ltd.). The composite hollow fiber membrane obtained was then subjected to heat treatment at 350°C in vacuo for 4 hours so that the amide amino acid component as a copolymerizable component was cyclized into imidazopyrrolone to obtain a composite hollow fiber membrane.

The composite hollow fiber membrane obtained was measured for oxygen and nitrogen permeation rates in the same manner as in Example 10. The oxygen/nitrogen separation factor calculated is set forth in Table 2.

#### EXAMPLE 18

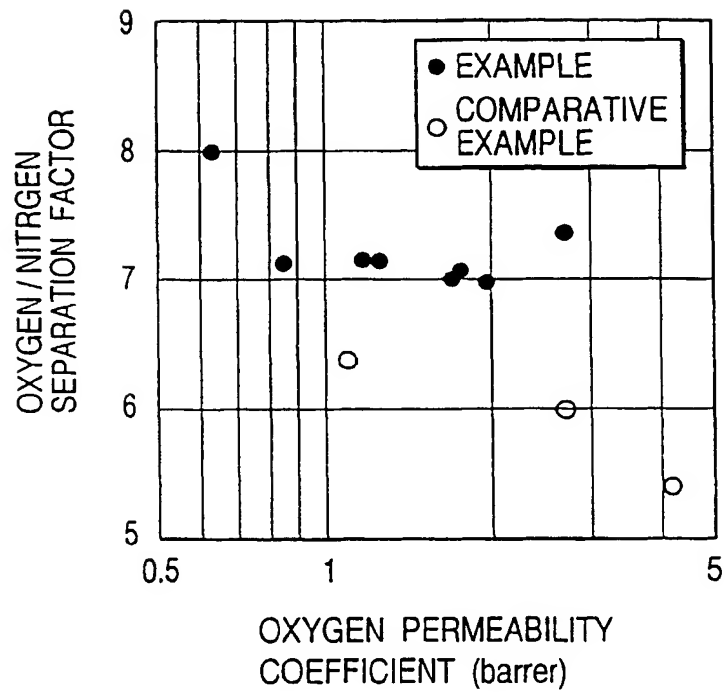
A composite hollow fiber membrane was obtained in the same manner as in Example 10 except that the polyhydrazidoimide resin obtained in Example 1 to be used as the resin for the spinning dope (a) was replaced by the polyhydrazidoimide resin obtained in Example 9 and the N-methylpyrrolidone solution of a polyimide ("MATRIMID 5218", available from Asahi-Ciba Limited) to be used as the spinning dope (b) was replaced by the same resin solution as used in Example 17.

The composite hollow fiber membrane obtained was measured for oxygen and nitrogen permeation rates in the same manner as in Example 10. The oxygen/nitrogen separation factor calculated is set forth in Table 2.

Table 2

		Gas permeation rate [ $\times 10^5$ cm <sup>3</sup> (STP)/cm <sup>2</sup> sec.cmHg]		Separation factor Oxy- gen/nitrogen
		Oxygen	Nitrogen	
Example	10	0.795	0.0995	7.99
	11	0.927	0.118	7.86
	12	0.873	0.109	8.01
	13	1.12	0.141	7.94
	14	1.03	0.129	7.98
	15	0.774	0.0974	7.95
	16	1.27	0.179	7.09
	17	2.41	0.329	7.33
	18	0.934	0.132	7.08

# FIGURE







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(74) Representative:  
Kraus, Walter, Dr. et al  
Patentanwälte Kraus, Weisert & Partner  
Thomas-Wimmer-Ring 15  
80539 München (DE)

(71) Applicant:  
**DAINIPPON INK AND CHEMICALS, INC.**  
**Itabashi-ku Tokyo (JP)**

(54) **Separation membrane**

(57) Separation membranes excellent in strength, durability, heat resistance and solvent resistance as well as in balance between substance separation properties and substance permeability are disclosed, which are formed from polyhydrazidoimide resins, and preferably comprises a non-porous dense layer formed from a polyhydrazidoimide resin obtained from the reaction of an aromatic tetracarboxylic dianhydride such as 4,4'-(hexafluoroisopropylidene)diphthalic anhydride and an aromatic dihydrazide such as isophthalic dihydrazide as essential components.

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